New chemical and isotopic data on the groundwater system of Bagno di Romagna, northern Apennines, Emilia-Romagna province, Italy

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ABSTRACT - The thermal spring and well exploited within the S. Agnese spa of Bagno di Romagna and the nearby cold Chiardovo spring were repeatedly sampled and analyzed for major ions and stable and radioactive isotopes of water.

Main results for the S. Agnese thermal waters are: (i) cations in solution are in partial chemical equilibrium with host rocks, (ii) K/Na geothermometry provides a temperature estimate of about 130°C for the geothermal reservoir, corresponding to about 3.5 km depth, (iii) a mean recharge altitude around to 1050 m a.s.l. for the hydrothermal circuit is estimated from oxygen isotopes, and (iv) a submodern age is supported by the tritium content.

The Chiardovo spring appears to be fed by shallow water, that mixes with rising deep water before emerging.

Key words: spring waters, Bagno di Romagna, major chemistry, stable isotopes, tritium.

Introduction

Chemical and isotopic studies are normally undertaken to obtain information on the hydrologic systems in terms of origin, recharge area and underground residence time of water, as well size and temperature of the aquifers at depth.

The present work deals with a number of thermal and cold groundwaters of Bagno di Romagna locality (479 m a.s.l.; Forlì district, Emilia-Romagna province), and represented by the thermal S. Agnese spring and BR5 well (108 m deep) both exploited within the S. Agnese spa, and the cold Chiardovo spring emerging at about 0.9 km from the spa and conveyed into the spa by a pipe (Fig. 1). Five water samplings were carried out from October 1996 to May 1997, and samples were ana-
Fig. 1 - Schematic map of the Bagno di Romagna area, with location of the studied waters. The grey area represents Marnoso-Arenacea terrains, and the white area Savio River alluvial deposits (modified from Martelli, 1991).

lyzed for major chemistry, hydrogen and oxygen compositions and tritium content. The Chiardovo spring was sampled at the emergence point and from the pipe within the spa.

The studied groundwaters occur in the Savio river valley in northeastern Apennines, and are known and exploited since Roman times. All waters are sulfurous, and oxidation of $H_2S$ to $S^\circ$ can be observed at the outlet of the Chiardovo spring. Previous chemical and isotopic data on the S. Agnese spring were published in current literature by Minissale (1991); they are fully consistent with those obtained in the present paper. Stable and radioactive isotope analyses were performed on a number of springs in the Bagno di Romagna and S. Piero in Bagno localities during 1980 and 1981 (Merlo et al., 1982), but the analytical results are not reported in the mentioned paper. Maximum flowrates in the range 8-9.4 l/s and temperatures of 42 to 43.5°C are reported by Merlo et al. (1982) for the S. Agnese spring throughout the hydrological year, and an interference between the spring and the shallow water system was noted.

**Geological and hydrogeologic outlines**

Bagno di Romagna is located in the exterior part of the northern Apennine segment known as «Appennino Romagnolo», about 50 km from the Adriatic Sea. The local stratigraphic edifice is constituted by overthrust units with faults and folds related to the compressive tectonics due
to the collision between the Adriatic and African plates, which started in Middle-Upper Eocene times and is still active nowadays (Castellarin et al., 1986; Capozzi et al., 1991). The foreedep dep basins were filled by turbiditic sediments of Oligocene to Miocene ages (Ricci Lucchi, 1986; Boccaletti et al., 1990).

The geology in the Bagno di Romagna area is dominated by the Marnoso-Arenacea Formation (feldsparic-micaeous-quartzose sandstones, marls, siltites and argillites; thickness of 1300 to 2500 m; Burdigalian-Tortonian). The uppermost Verghereto member of the formation, constituted by marly terrains with a thickness 500 m, is in sharp contact with the overlying Savio Valley Complex (upper Cretaceous to Langhian; e.g. Merlo et al., 1988; Martelli, 1994). This complex is formed by clays and marly clays with chaotic structure and other different rocks (limestones, marls, sandstones, siltites, cherts) similar to those of the Liguarian and Epiligurian sequences; outcrops are over 400 m thick (Benini et al, 1991), and total thickness reaches about 1000 m according to geophysical surveys (Martelli, 1994). The Marnoso-Arenacea Formation lies on terrains of the Tuscan Series (argillites, siltites, sandstones and marls; upper Cretaceous to Aquitanian; thickness up to 1000 m), which in turn are underlain by a Mesozoic carbonate substratum (e.g. Ten Haaf and Van Wamel, 1979), the top of which should be placed at about 4000 m depth beneath Bagno di Romagna (e.g. Merlo et al., 1982; see also Martelli, 1994). Tectonic structures in the area are represented by folds and faults related to the compressional movements, and important transcurrent faults related to a disjunctive phase (e.g. Merlo et al., 1982). The dominant structural element nearby the thermal zone is the S. Piero syncline, an Apennine depression filled with allochthonous rocks. Additional and much more detailed information on geology of Romagna can be found in Martelli (1994 and references therein).

The conceptual hydrothermal circulation model for the S. Agnese water is shown in Fig. 2. The recharge area is placed in the permeable outcrops of the Savio Valley Complex (about 1000 m elevation a.s.l.), the hydrothermal circulation is restricted within the Marnoso Arenacea down to a minimum depth of 1500 m, and the emergence point occurs in correspondence of deep tectonic structures. Salinity in studied thermal waters is less than 1 g/l, that is much lower than that of 30-70 g/l measured for water in the carbonate substratum as from exploratory oil drilling logs (Martelli, 1994). The residence time of water in the underground was estimated to be more than 30 years, and possibly few hundred years (Merlo et al., 1982). Infiltrating water is heated by normal geothermal gradient (33°C/km; Martelli, 1994), then underwent cooling during its ascent towards the surface and likely mixes with shallow cold water before emerging (Martelli, 1994).

Average petrographic composition of the Marnoso-Arenacea at Bagno di Romagna (Gandolfi et al., 1983) is basically controlled by quartz (37% by weight), carbonate cement (20%) and plagioclase (15%), followed by micas/chlorites (10%) and K-feldspar (5%). In the carbonate cement the dolomite to calcite by weight ratio averages 0.2. Limestone fragments (5%) and dolostone fragments (1%) are also present.
Fig. 2 - Geological-structural cross-section and hydrothermal circulation in the Bagno di Romagna area (modified from Merlo et al., 1988).
Analytical procedures

Temperature and pH of waters were measured just after collection. Calcium, magnesium, sodium and potassium in solution were determined by atomic absorption spectrophotometry. Sulfate was analysed by turbidimetry/spectrophotometry, nitrate by colorimetry after reduction to nitrite, chloride and bicarbonate by means of specific IDRIMETER kits supplied by Carlo Erba. Bicarbonate was analysed in the lab within few hours after sampling. TDS was determined by summing the concentrations of the analysed ions.

The hydrogen and oxygen isotopic compositions (\(^{2}H\) and \(^{18}O\), in ‰, relative to V-SMOW standard) were determined, respectively, by reaction of water with metallic Zn at 500°C (Kendall and Coplen, 1985) and by equilibration of CO\(_{2}\) with water at 25°C (Epstein and Mayeda, 1953), then submitting H\(_{2}\) and CO\(_{2}\) to mass-spectrometric analysis. The standard deviation of runs was within ±0.1‰ for oxygen and ±1‰ for hydrogen. Tritium in water was measured following basically the method of Cameron (1967), and values are given in tritium units (TU), the number of tritium-atoms relative to \(^{1}H\) hydrogen-atoms. Accuracy of results was normally within ±1TU.

Results and discussion

The chemical and isotopic results on studied waters are reported in Tab. 1.

Chemical results

The main chemical results can be summarized as follows: (1) waters are of Na-HCO\(_{3}\) type (Fig. 3), with thermal water much richer in Na and HCO\(_{3}\) with respect to cold water. In addition, Na is considerably depleted relative to HCO\(_{3}\)- but largely in excess with respect to Cl; (2) HCO\(_{3}\) is much more abundant than Ca and Mg; (3) SO\(_{4}\) is low or absent, but waters smell of H\(_{2}\)S; and (5) both cold and thermal waters appear to be immature in the anion

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<th>Eh (mV)</th>
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<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>K HCO(_{3})</th>
<th>SO(_{4})</th>
<th>Cl</th>
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*Chemical data are in mg/l; n.a. = not analysed; n.d. = undetectable.*
Fig. 3 - Trilinear diagrams for major anions and cations in water samples, in mg/l. Enlargements are also provided. All waters are high in alkalies (sodium) and bicarbonate. In the anion diagram, all samples are out the shaded box expected for equilibrated (mature) geothermal waters (Giggenbach, 1988). Data on seawater in this and following figures refer to a southern Tyrrhenian Sea sample (Cortecci et al., 2000).
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trilinear diagram of Fig. 3. Waters can be classified as meso-mineral, according to their TDS values (Celico, 1986).

Based on the Na-K-Ca-Mg diagram of Fig. 4 (Giggenbach, 1988), the thermal water samples from S. Agnese spring and BR5 well appear to be partially equilibrated with rocks. Cold water from Chiardovo spring lies close to the boundary between the nonequilibrium field and the partial equilibrium field. The Mg/K and Mg/Na ratios in the waters (Figs. 5a, b) are in the order lower and higher with respect to equilibrium with relevant minerals at the emergence temperatures, and much higher than expected for isochemical dissolution of the Marnoso-Arenacea. These features agree with the immature character of the waters, and in particular support that in the thermal waters an appreciable fraction of Mg in solution may derive from dissolution of dolomite during ascent of the water from the geothermal reservoir. This interpretation agrees with the observation that in many samples Mg and Ca are nearly equivalent. The Na/K ratios are within the K-feldspar stability field (Fig. 5c), thus explaining the low K content in the waters relative to Na.

The chemical relation between thermal and cold water samples in the cation diagram of Fig.3 suggests that the Chiardovo
Fig. 5 - Comparison of the Na, K and Mg mole ratios in water samples with those expected in equilibrium with relevant mineral assemblages at the outlet temperatures, and in highly immature solutions resulting from the isochemical dissolution of the Marnoso-Arenacea. The PRHEEQC computer program (Parkhurst, 1995) was used for calculating ion activities. The calculation of the equilibrium mineral-mineral lines was performed according to Giggenbach (1988 and references therein).
water may be a mixture of rising thermal water poor in Ca and Mg with shallow cold water enriched in Ca (± Mg), the proportion of the shallow component being predominant. The lower Mg and Ca contents in the Chiardovo water from the pipe with respect to the emergence may be ascribed to deposition of carbonate as a consequence of CO$_2$ degassing during transport.

The excess of HCO$_3$ in the studied waters with respect to Ca and Mg can be related to contributions of CO$_2$ from a deep-seated source (Minissale, 1991), as well as to oxidation of organic matter during bacterial reduction of aqueous SO$_4$ (e.g. Thode, 1991). The presence of H$_2$S (and the low to null content of SO$_4$) supports that sulfate-reducing bacterial activity is operating in the groundwaters of Bagno di Romagna. The appreciable amount of SO$_4$ in the Chiardovo spring may be due to oxidation in shallow water of sulfide sulfur carried by deeper water. This interpretation agrees with the pH (mean 8.8) and Eh (mean -183 mV) values in the water, which are appropriate for inorganic oxidation of HS$^-$ to SO$_4$ (e.g. Faure, 1998). The pH (mean 8.3) and Eh (mean -204 mV) values in the S. Agnese and BR5 waters are lower, thus precluding the oxidation of HS$^-$ to SO$_4$.

As far as the temporal variations are concerned, the chemical parameters appear to be in general fairly constant, considering the low concentration values and the relatively high analytical uncertainties. Major exception is represented by SO$_4$ in the Chiardovo spring, that may be explained with variable contributions of sulfate from sulfide oxidation. Noteworthy is the constancy of K in the thermal water samples, thus testifying the control by the K-feldspar mineral phase. K is also constant in the cold water samples, but its concentration is lower possibly due to dilution effects.

**Chemical geothermometry**

S. Agnese and BR5 thermal waters are immature as defined by Giggenbach (1988 and 1997), both in terms of anion composition (see Fig. 3) and cation composition, that is their maturity index $MI = 0.315 - \frac{\log (c_{K^2}/c_{Mg})}{\log (c_{K^2}/c_{Na})}$, with $c = \text{mg/l}$, is definitively lower than 2 (Giggenbach, 1988). Therefore, the application of the K/Mg and K/Na geothermometers is problematic. The K/Mg thermometer should be rejected not only because the K/Mg ratio acquired by water at depth may have been modified due to the adjustment of Mg at lower temperature during ascent, but also considering that Mg in the water may derive appreciably from dolomite dissolution (a retrograde process) in addition to silicate minerals hydrolysis. On the other hand, the K/Na ratio acquired at depth may have been basically preserved (see Giggenbach, 1997). Calculated temperatures by the K/Na thermometer (Giggenbach, 1988) are in the range 111 to 135°C (on average 126°C), and correspond to a depth of 3-3.5 km for the geothermal reservoir. Quite comparable thermometric estimates of 103 to 112°C are obtained for the Chiardovo cold water, such a consistency suggesting that this water is a binary mixture of deep water and shallow water, with the resulting K/Na ratio being controlled by the deep component. The assumption on the preservation of the K/Na is supported by inspection of Fig. 6, where the Mg/Ca...
and K/Na ratios in the studied waters are compared with those expected from the Marnoso-Arenacea isochemical dissolution and the water-rock full equilibration at different temperatures. The position of the S. Agnese and BR5 thermal waters can be interpreted in terms of departure from the equilibrium state established in the geothermal reservoir, due to addition of Mg in the water during ascent towards the surface. On the other hand, the K/Na ratio in the water appears to have kept nearly constant from the reservoir to the surface.

Isotopic results

The δ¹⁸O and δD values of the S. Agnese spring and BR5 well waters are indistinguishable, with averages of -8.5‰ and -55.0‰, respectively. These isotopic val-
ues are nearly identical, even if a slightly lower, with those of the Chiardovo water ($\delta^{18}O = -8.3\%o$ and $\delta^2H = -54.4\%o$). Excluding a common recharge altitude for the S. Agnese thermal water and the Chiardovo cold water, their $\delta^{18}O$ and $\delta^2H$ consistency can be interpreted in terms of depletion in $^{18}O$ and $^2H$ of the shallow (cold) component as a consequence of mixing with the rising deep (hot) component. The $^3H$ content in the S. Agnese water is practically zero (0 to 0.3 T.U.), thus denoting a submodern recharge prior to 1952 (e.g. Clark and Fritz, 1997). The Chiardovo water is enriched in $^3H$ by 1.6 T.U., this supporting mixing between endmembers from submodern and recent recharge. For comparison, the $^3H$ content in monthly precipitation at Bologna (about 80 km from Bagno di Romagna, on the western side of the

![Graph](image_url)

**Fig. 7 -** Stable isotopes in water samples, compared with the global meteoric water line with deuterium excess $d = 10\%o$, the meteoric water line at Bologna ($d = 10.4\%o$; Panettiere, 1998) and the meteoric water line for the eastern Mediterranean area ($d = 22\%o$). Data on seawater are from Cortecci et al. (2000).
Appennino Romagnolo) was in the range 7.2 to 19.4 T.U. (on average 11 T.U) during 1996-1997 (Panettiere, 1998).

Studied waters are meteoric in origin and their deuterium excess (d = δH - 8°O, as defined by Dansgaard, 1964) ranges between 11 and 14‰ (10.4‰ for precipitation at Bologna; Panettiere, 1998), in keeping with an origin of the water mainly from condensation of oceanic vapor (d = 10‰ for the global meteoric water line GMWL; e.g. Clark and Fritz, 1997), possibly a slightly «contaminated» by condensed Mediterranean vapor (d = 22‰ for rainwater in the eastern Mediterranean areas; Gat and Carmi, 1970) (Fig. 7). Alternatively, the dispersion of the data points on the left of the GMWL (Fig. 7) can be interpreted as due to isotopic exchange of water with CO₂ and H₂S (e.g. Clark and Fritz, 1997). Significant isotopic shifts due to interaction of water with rocks at depth can be excluded, likely because of the low enthalpy of the fluids and possibly the high water to rock ratio in the reservoir.

The δ¹⁸O signature of S. Agnese and BR5 well thermal waters is lower by 3‰ than expected for precipitation at sea level in the Adriatic area of interest (Zuppi and Bortolami, 1982), that is about -5.5‰, with an isotopic altitude gradient of -0.28‰/100m. This isotopic depletion corresponds to a recharge altitude of 1050 m a.s.l., that can be placed in the Savio Valley Complex outcrops (Fig.2).

Finally, the temporal constancy of the δ¹⁸O (and δH) values in both thermal and cold spring waters is noteworthy, this possibly indicating a relatively large size of the aquifers or simply a long residence time (i.e. a slow circulation rate) of water in the underground or both, so that the seasonal isotopic variations in the recharge precipitation are virtually cancelled.

**Conclusions**

The chemical and isotopic data here presented and discussed support the conceptual circulation model nowadays in use for the hydrothermal system of Bagno di Romagna.

New constraints obtained within this work deal with (1) the temperature and depth of the geothermal reservoir, estimated to be close to 130°C and approaching 3.5 km, respectively; (2) a recharge altitude of 1050 m a.s.l. for the hydrothermal circuit, and (3) a submodern age for thermal waters exploited within the S. Agnese spa. In addition, the isotopic seasonal variations expected for the meteoric recharge are virtually cancelled, in keeping with the relatively old age of water and possibly a large geothermal reservoir at depth.

Excluding a common recharge altitude for the S. Agnese thermal spring and the Chiardovo cold spring, their δ¹⁸O and δH consistency can be interpreted in terms of depletions in δ¹⁸O and δH of the shallow (cold) component as a consequence of mixing with the rising deep (hot) component.

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